# A PILOT STUDY OF THE PARTIAL NITRIFICATION/COMPLETE DENITRIFICATION PROCESS

By

CHIE-CHIEN TSENG

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Abstract of Dissertation Presented to the Graduate School
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## A PILOT STUDY OF THE PARTIAL NITRIFICATION COMPLETE DENITRIFICATION PROCESS

By

CHIE-CHIEN TSENG

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Chairman: Ben Koopman
Major Department: Environmental Engineering Sciences

The results of computer modeling and experimentation with a bench-scale experimental system have shown that a novel process for partial nitrification/complete denitrification (PN/CD) can achieve nitrogen removal equivalent to that obtained with the Ludzack-Ettinger (LE) process. Based on modeling results, the PN/CD process reduces aeration energy costs by up to 16% and energy requirements for recirculation and recycle pumping by up to 28% relative to the LE process. Furthermore, the total reactor volume of the PN/CD process is 24 to 44% less than that required by the LE process for equivalent nitrogen removal. The bench-scale PN/CD process was operated to confirm the feasibility of the proposed approach. The wastewater feed to this system was settled domestic sewage supplemented with ammonia and acetate. The experimental

[illegible] [illegible] successfully achieved partial nitrification with effluent ammonia concentrations of 5 to 9 mg/L and also met a 12 mg/L discharge limit on total nitrogen. This effluent nitrogen composition is appropriate for wastewater reused in agriculture and landscape applications where high ammonia nitrogen concentrations are acceptable. Relative concentrations of ammonia and nitrate in the effluent were successfully controlled by varying the rate of mixed liquor recirculation. Process performance was insensitive to the dissolved oxygen concentration maintained in the oxic reactors.

The PN/CD process was also tested experimentally at the bench scale with different wastewater compositions over a range of influent ratios of chemical oxygen demand (COD) to total Kjeldahl nitrogen (TKN). Mean ammonia nitrogen concentrations in PN/CD process effluent varied from 6.5 to 8.4 mg/L at influent COD/TKN ratios varying from 3.7 to 8.8. Ammonia nitrogen concentrations in the influent wastewater had little effect on effluent ammonia levels. Bleed-through of COD to the effluent was not noticed at influent filterable COD/ammonia N ratios between 2 and 11. Denitrification was nearly complete (mean effluent nitrate plus nitrite N < 1.4 mg/L) at influent COD/TKN ratios of 5.3 or greater, whereas nitrate and nitrite accumulation occurred at lower ratios. The denitrification performance of the pre-anoxic reactor of the PN/CD process was consistent with that of other pre-denitrification processes when compared in terms of [illegible]

oxidized nitrogen

# CHAPTER 1
# INTRODUCTION

As demand for water reuse through agricultural and landscape application expands, increasing numbers of treatment works are facing requirements for partial nitrogen removal. Agricultural and landscape application is the primary use of reclaimed wastewater in several states (Arizona, California, Colorado, Florida, Texas) and in some regions accounts for 70-85% of treated municipal wastewater (Arber, 1991). The 1992 inventory of reclaimed water projects in Florida had a permitted capacity of 26 $m^3/s$, which is 30% of the state's total permitted wastewater treatment capacity (York and Potts, 1995). When wastewater is land applied, partial removal of nitrogen is often required to prevent concentrations of nitrate nitrogen in the receiving aquifer from exceeding the federal maximum contaminant level for drinking water (10 mg/L $NO_3$-N). Appropriate target concentrations for effluent nitrogen in such cases can be based on the total nitrogen content of the reuse water where soil conditions are conducive to nitrification of effluent as it percolates through the soil to the groundwater. Under these conditions, any combination of nitrogen species (ammonia, nitrate, organic nitrogen) [illegible] than the target effluent total nitrogen [illegible] is permissible. Allowing for plant uptake and [illegible] nitrogen in the soil column, a target effluent total nitrogen concentration of 12 mg/L is typically sufficient to ensure that the maximum contaminant level of nitrate nitrogen in the groundwater is not exceeded. This requires 50-70% removal of nitrogen from municipal wastewaters with typical total Kjeldahl nitrogen concentrations of 25 to 40 mg/L.

Partial nitrogen removal in the activated sludge process is usually achieved by nitrification of all available wastewater nitrogen to nitrate, followed by partial removal of the nitrate through denitrification. It would be just as acceptable to oxidize only a fraction (however much is necessary) of the influent ammonia to nitrate and then to denitrify completely before discharge. The latter approach requires less oxygen and less nitrifying biomass, which reduces energy consumption, reactor volumes, and aeration system capacity. Another benefit of partial nitrification/complete denitrification is that there will be a smaller net consumption of alkalinity. This is important in nitrogen removal facilities treating wastewater with relatively low alkalinity concentrations. Finally, with 6 to 8 mg/L ammonia nitrogen in the effluent, a combined, rather than free, chlorine residual is formed through the chlorine disinfection process This reduces the sensitivity of chlorine demand to variations in ammonia concentration and decreases chlorine consumption (Matson et al., 19[illegible]).

The objective of this study was to evaluate the feasibility of a novel single-sludge process for meeting an effluent limit of 12 mg/L total nitrogen while minimizing the extent of ammonia oxidation Computer modeling was carried out to compare the partial nitrification/complete denitrification (PN/CD) process to a process for partial nitrogen removal that is now widely used (the Ludzack-Ettinger process). The ability to control hydraulically the relative concentrations of ammonia and oxidized nitrogen (nitrate and nitrite) in PN/CD process effluent was tested using a bench scale system The sensitivity of process performance to variations in the influent ratio of chemical oxygen demand to total nitrogen (COD/N ratio) and influent ammonia concentration were also determined experimentally.

# CHAPTER 2
# LITERATURE REVIEW

## Water Reuse for Irrigation and Groundwater Recharge

Although wastewater reclamation has been traditionally practiced for pollution control, benefits obtained from used of reclaimed water to supplement available water resources have become increasingly important. Uses of reclaimed water include indirect potable reuse, agricultural reuse, urban landscape irrigation, industrial reuse, groundwater recharge, and potable reuse. Before it can be used for unrestricted irrigation, wastewater must be treated to meet agronomic, public health, and aesthetic requirements. This usually means reduction of nitrogen concentration to less than 10 mg/L in addition to removal of pathogenic microorganisms and parasites and essentially complete removal of suspended solids and biodegradable organic carbon (Bouwer, 1991). Nitrogen removal is also important when reclaimed water is ultimately used for supplementing municipal drinking water supplies (EPA, 1992). High concentrations of nitrate nitrogen in drinking water supplies may have adverse effects on human health, including methemoglobinemia and cancer. The maximum contaminant level (MCL) for nitrate nitrogen in public drinking water supplies

United States is 10 mg/L. This same concentration [illegible] is required in the State of Florida for drinking water (FDER, 1989).

Agricultural irrigation is estimated to consume [illegible] percent of the total water demand nationwide (Solley et al., 1988). In some western states (Montana, Colorado, Idaho, and California) with significant agricultural production, the percentage of fresh water used for irrigation is substantially greater, accounting for up to 90 percent of their total fresh water withdrawals (Solley et al., 1988).

A significant portion of existing water reuse systems supply reclaimed water for agriculture irrigation. In Florida, agriculture irrigation accounts for approximately 34 percent of the total reclaimed water used within the state (FDER, 1990). In California, nearly 63 percent of the total reclaimed water is used for agriculture irrigation (California State Water Resource Control Board, 1990). Recent values reported for reclaimed water use for agriculture irrigation in Florida, California, and Texas were 50, 150, and 290 Mgal/d, respectively (EPA, 1992).

Besides irrigation, reclaimed wastewater is also an important source of water for groundwater recharge programs. Uses include (1) establishment of saltwater intrusion barriers in coastal aquifers, (2) provision of further treatment for water reuse, (3) augmentation of potable or [illegible] [illegible], storage of reclaimed water, and [illegible] [illegible] of ground subsidence (WPCF [illegible]).

Biological Nitrogen Removal in Activated Sludge Processes

Municipal wastewater treatment systems designed for nitrogen removal usually consist of carbon oxidation, nitrification, and denitrification. Nitrification in the activated sludge process is accomplished by designing the process to operate at a solids retention time that is long enough to prevent the slow-growing nitrifying bacteria from washing out of the system. In biological denitrification, nitrate nitrogen is used by a variety of facultative heterotrophic bacteria as the electron acceptor in the absence of dissolved oxygen while carbonaceous compounds are used as the electron donors. Then, nitrate nitrogen is converted to nitrogen gas which escapes to the atmosphere.

Activated processes for nitrogen removal can be classified into separate-sludge systems and single-sludge systems. Separate-sludge systems operate carbonaceous oxidation and nitrification separately, providing excellent protection of the nitrification step against toxicants (Metcalf & Eddy 1991). Single-sludge systems operate without intermediate clarifiers, offering advantages in terms of lower capital costs for secondary clarifiers, reduction of external carbon source requirements, and overall lower consumption of alkalinity. Single-sludge processes for nitrogen removal have also proven to be stable in operation while providing a wide variety of configurations for achieving varying levels of nitrogen removal. Further discussion of biological nitrogen removal processes will therefore focus on single-sludge processes.

Single-sludge nitrification-denitrification systems are usually classified according to their flow regime, stage of anoxic and aerobic sequences, or method of aeration. In subsequent discussion, the term *anaerobic* will be used to denote an environment effectively devoid of either dissolved oxygen, nitrate, or nitrite. The term anoxic will be used to refer to an environment that is effectively devoid of dissolved oxygen, but which has nitrate or nitrite (or both) present. Finally, the term oxic (or aerobic) will be used to denote an environment that has dissolved oxygen present.

## Single Anoxic Zone Processes

The earliest investigation of single-sludge nitrification-denitrification process for domestic wastewater was by Wuhrmann (Ekama et al., 1984). The Wuhrmann process (Fig. 2-1) placed a single denitrification reactor after a combined carbon oxidation-nitrification reactor and returned the settled sludge to the aerobic reactor and can therefore be referred to as a post-denitrification process. Although not widely used in its [illegible] configuration, the Wuhrmann process may be recognized as an integral component of the popular dual [illegible] processes

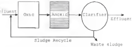


Figure 2-1  Schematic of Wuhrmann process [redrawn from Wuhrmann (1962)]

The process developed by Ludzack and Ettinger differed from the Wuhrmann process by placing the anoxic reactor ahead (upstream) of the aerobic reactor (Ludzack and Ettinger, 1962) and is thus referred to as a predenitrification process (Fig. 2-2). Nitrate nitrogen combined with settled sludge are recycled to the anoxic zone where they mix with the external carbon source provided by raw wastewater. Ludzack and Ettinger (1962) recognized that the denitrification rate would be limited by the sludge recycle rate because conventional sludge recycle rate (30-100 % of influent) does not provide enough nitrate to optimize denitrification. They therefore provided for recirculation of nitrified mixed liquor to the anoxic reactor, using the sludge recycle line as a conduit.

Barnard ([illegible]) later proposed complete separation of the anoxic and oxic reactors and use of a separate pipe for mixed liquor recirculation. This configuration became know as the 'modified Ludzack-Ettinger process" by other South African researchers (Ekama et al., 1984).

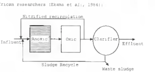


Figure 2-2. Schematic of Ludzack-Ettinger process [redrawn from Ludzack and Ettinger (1962)]

The anaerobic/anoxic/oxic (A /O) process was modified from the anaerobic/oxic (A/O) process originally developed for sludge bulking control and biological phosphorous removal. In the A /O process, an anoxic reactor is placed between the anaerobic reactor and the oxic reactor (Fig. 2-3). Nitrified mixed liquor is recirculated to the anoxic reactor whereas settled returned sludge is directed to the head of the anaerobic reactor. Although the anaerobic reactor is not required for nitrogen removal, it is useful as an anaerobic selector to suppress the filamentous bacteria in the system, as well as to promote biological phosphorus removal.

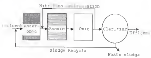


Figure 2-3 Schematic of A²/O process [redrawn from EPA, (1993)]

The University of Capetown (UCT) process was developed at the University of Capetown in South Africa (Fig. 2-4). The UCT process differs from the $A^2/O$ process by rerouting the sludge recycle line to the anoxic reactor and adding an internal recirculation line from anoxic reactor to the anaerobic reactor. By returning the settled sludge to the anoxic reactor, the introduction of nitrate to the anaerobic reactor is eliminated. This improves the biological release of phosphates in the anaerobic reactor, which is prerequisite to excess biological phosphate uptake in the anoxic and oxic reactors.

The reaeration-denitrification-nitrification (R-D-N) process (Fig. 2-5) was developed to reach the same level of nitrogen removal of the pre-denitrification process with lower volume requirements (Wanner et al., 1990). A reaeration reactor is added to completely nitrify the ammonia nitrogen in the underflow of the secondary clarifier The high concentration of mixed liquor suspended solids in the reaeration reactor enables the R-D-N process to oxidize the same amount of ammonia nitrogen with less reactor volume.

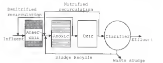


Figure 2-4 Schematic of UCT process [redrawn from EPA, (1993)]

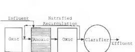


Figure 2-5 Schematic of R-D-N process [redrawn from Wanner et al. (1990)]

## Multiple Anoxic Zone Processes

The four-stage Bardenpho process (Fig. 2-6) integrates a Ludzack-Ettinger process (the first two reactors) with a Wuhrmann process (the second and third reactors). The final reactor serves mainly to strip dissolved nitrogen gas from the mixed liquor before it enters the secondary clarifier. The second anoxic reactor removes additional nitrate through endogenous denitrification, allowing the four-stage Bardenpho process to achieve higher levels of nitrogen removal than the single anoxic zone processes.

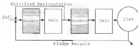


Figure 2-6 Schematic of four-stage Bardenpho process [redrawn from EPA (1993)]

The modified UCT process adds a second anoxic reactor between the anoxic and aerobic reactors of the UCT process (Fig 2-7). The first anoxic reactor is designed to denitrify all the nitrate nitrogen recycled from clarifier. The second anoxic reactor is sized to denitrify the nitrate nitrogen recycled from the first oxic reactor. The modified UCT process eliminates the introduction of nitrate nitrogen o the anaerobic reactor, hence optimizing biological phosphorus removal efficiency. With part of the readily biodegradable COD being consumed in the first anoxic reactor, the specific denitrification rate in the second anoxic reactor will be lower than in the first anoxic reactor.

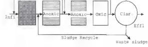


Figure 2-7 Schematic of modified UCT process [redrawn from EPA (1993)]

To accomplish nitrification-denitrification without recirculating mixed liquor, wastewater can be introduced to multiple anoxic zones within the oxic reactor. This configuration is referred to as the modified step-feed process (Fig. 2-8). In this process, each oxic zone is sized to completely nitrify the influent ammonia discharged to that zone. The anoxic zones are sized to completely denitrify the nitrate nitrogen produced from the preceding oxic zone. In addition to saving energy associated with mixed liquor recirculation, the step-feed process also decreases reactor volume requirements, since the mixed liquor suspended solids (MLSS) concentrations near the upstream end of the reactor are higher than those at the downstream end, thus giving higher nitrification and denitrification rates.

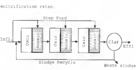


Figure 2-8 Schematic of modified step-feed process [redrawn from EPA (1993)]

Oxidation ditches can be operated to create one or more anoxic zones throughout the length of a channel. This depends on the number of aerators in each channel, their speed ranges, and oxygen transfer capacity. An example of an oxidation ditch is shown in Figure 2-9. In this case, the feed is introduced at a point in the channel which is the greatest distance from the upstream aerator. This helps ensure that the zone of wastewater input will be anoxic. A second anoxic zone may occur upstream of the second aerator, depending on the oxygen uptake rate of the mixed liquor

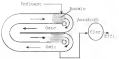


Figure 2-9. Schematic of oxidation ditch process operated to achieve nitrogen removal in the ditch [redrawn from [illegible] (1993)]

### Periodically Aerated Processes

A succession of aerated and unaerated phases are used in a sequencing batch reactor (SBR) for nitrogen removal (Fig. 2-10). Since the relative length of each phase and the total cycle time can be readily varied, SBRs are very flexible in their operation. Another periodically operated process is the Bio-Denitro process, which is one example of phased isolation ditch technology. Figure 2-11 depicts the four phases (A, B, C, D) of the Bio-Denitro process. Like SBRs, this process has the ability to vary the length of each phase as well as the total time to cycle through all four phases. Hence, operation of this system can be optimized to account for seasonally varying flows, wastewater composition, and temperature. A continuous flow through the system is always maintained. Of course, the aeration in any activated sludge process that nitrifies can be cycled on and off to create periods of anoxic conditions for nitrogen removal. Operational modifications to enable cyclical aeration has been especially popular for package plants that dispose of their treated effluent by land application. Many of these facilities in the State of Florida have had to implement cyclical aeration for nitrogen removal to avoid nitrate contamination of surficial aquifers underlying their land application sites (personal communication, George McDonald, Berryman & Henigar, Crystal River, FL, 1996).

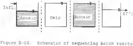


Figure 2-10. Schematic of sequencing batch reactor (SBR) for biological nitrogen removal [redrawn from EPA (1993)]

## Performance of Single-sludge Processes for Nitrogen Removal

The performance of a number of different single-sludge processes for nitrogen removal is reviewed in Table 2-1. The major categories of processes are ranked according to nitrogen removal efficiency. As can be seen, the multiple anoxic zone processes (e.g., Bardenpho, oxidation ditches, modified step feed) have the potential to achieve very high (up to 97%) nitrogen removals. Single anoxic zone processes

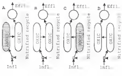


Figure 2-11. Four phases of operation for Bio-Denitro process [redrawn from Bundgard et al. (1989)]

are generally less efficient, achieving up to 85% removal. Cyclically aerated processes appear to have a nitrogen removal capacity on the same order as the single anoxic zone processes. One characteristic in common for all of the processes summarized in Table 2-1 is the relatively low effluent ammonia nitrogen concentrations that are produced. Although the range of effluent ammonia nitrogen concentrations is wide (0.1-8.4 mg/L), most of the reported values are quite low, as reflected by a median effluent ammonia nitrogen concentration of 1.5 mg/L. In fact, for most of these processes (those with nitrification taking place in main stream reactors), it would be difficult to operate dependably at substantially higher effluent ammonia levels. This is because the onset of nitrification with respect to solids retention time is very sharp, as shown in

Table 2.1 Effect of COD/N ratio on nitrogen removal in completely nitrifying, single-sludge processes with pre anoxic reactors

| Process | Capacity | Influent COD/TN | Influent TN, mg/L | Effl TN, mg/L | TN removal, % | Effl NH, N, mg/L | Reference |
|---|---|---|---|---|---|---|---|
| A²/O | 133,000 p.e.¹ | 9.5 | 35 | 5.25 | 85 | 0.5 | de Wet et al (199 |
| A²/O | pilot plant | 5.5 | 57 | 16.4 | 66.75 | 0.26-0.77 | Kujawa Grelak and Ren |
| Bardenpho | pilot plant | 13.1 | 38.1 | 3.1 | 92.4 | | Barnard and Meiring (1 |
| Bardenpho | 12,500 m³/d | 7.8 | 24.2 | 1.8 | 91 | | EPA (1993) |
| Bardenpho | 500 p.e. | 10.8 | 43.4 | 5.9 | 87 | 0.3 | Heide (1977) |
| Bardenpho | 50,000 m³/d | 7.5 | 36.0 | 15.6 | 57 | 1.6 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 9.4 | 33 | 13.2 | 60 | 1.5 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 9.5 | 39 | 9.7 | 74 | 5.8 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 10.5 | 38 | 13.1 | 65.5 | 7.6 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 15.6 | 34 | 4.9 | 85.6 | < 1 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 8.7 | 31 | 12.2 | 60.1 | 3.5 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 12.1 | 39 | 10.3 | 73.6 | 4.7 | Pitman et al (1983) |
| Bardenpho | 50,000 m³/d | 6.15 | 39 | 19.1 | 48.8 | - | Nichells et al (1985) |
| Biodenitro | 2,400 m³/d | 8.3 | 30 | 5.3 | 81 | 0.74 3.0 | Tholander (1977) |
| Cyclical aeration | N/A | 9.3 | 21.3 | 5.2 | 76 | 1.0 | Heidman (1976 |
| Cyclical aeration | 1820 m³/d | 10.5 | 39.9 | 8.4 | 80 | 1.4 | Schwinn et al |

p.e. = population equivalent

Reported by authors as "nil"

Table 2-1 (continued)

| Process | Capacity | Influent COD/TN | Influent TN, mg/L | Effl TN mg/L | TN removal % | Effl $NH_4$-N mg/L | Reference |
|---|---|---|---|---|---|---|---|
| ISAM | 120,000 p.e. | 9.3 | 56 | 11.4 | 80 | 4.2 | Seyfried and Hartw[illegible] [illegible] |
| Ludzack-Ettinger | 3500 $m^3/d$ | 7.7 | 44 | 10.1 | 77 | 2.7 | Meat et al. (1985) |
| Ludzack-Ettinger | 130,000 $m^3/d$ | 6.3 | 20.6 | N/A | 40 | 1.2-3.7 | Plaza et al. [illegible] |
| Modified step feed | 60,500 $m^3/d$ | 11.9 | 19.4 | 1.8 | 91 | 0.3 | Applegat[illegible] |
| Modified step-feed | 100,000 p.e. | 16 | 55 | 7 | 83-92 | 1.0 | Kayser e[illegible] |
| R-D-N | 106 $m^3/d$ | 9 | 35.7 | 16.3 | 54.3 | 1.6 | de la Sota [illegible] |
|  | 67 $m^3/d$ | 8 | 33.3 | 14.3 | 57.6 | 3.8 | de la Sota et [illegible] |
|  | 43 $m^3/d$ | 9.6 | 49.6 | 17.6 | 64.5 | 3.5 | de la Sota et [illegible] |
| Oxidation ditch | 10,000 p.e. | 9.9 | 37 |  | 85 | 0.3 | Henze M 1991 |
| Oxidation ditch | 150,000 p.e. | 13.2<br>16.0 | 24<br>36 | 4<br>4 | 88<br>87 | 3.8<br>2.7 | Matsche and [illegible] |
| Oxidation ditch | 13,250 $m^3/d$ | 10 | 25 | 0.64 | 9[illegible] | 0.3 | [illegible] |
| Oxidation ditch | 14,400 $m^3/d$ | 12.2 | 16.6 | [illegible] | [illegible] |  | [illegible] |
| Oxidation ditch | [illegible]0,000 p.e. | 12 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

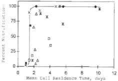


Figure 2-12. Effect of solids retention time on nitrification efficiency in a main stream reactor [redrawn from Grady and Lim (1980)]

Figure 2-12 (Grady and Lim, 1980). Only processes with side-stream nitrification reactors, such as the R-D-N process, can reliably operate with much higher effluent ammonia N levels. This point will be covered in more detail in Chapter 3.

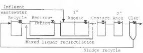
## The Partial Nitrification/Complete Denitrification Process

The partial nitrification/complete denitrification (PN/CD) process was first proposed by Potter (1993) for partial nitrification and complete denitrification of wastewater. Because this process carries out nitrification in side-stream reactors and oxidizes a minimum amount of ammonia, it is capable of achieving an acceptable level of nitrogen removal with less reactor volume and aeration energy requirements than traditional biological nitrogen removal processes such as the Ludzack-Ettinger process.

As shown in Figure 2-13, the PN/CD process includes a *primary anoxic reactor* (divided into two reactors-in-series to improve reaction kinetics) upstream of a short-retention time, aerated contact reactor. Denitrification takes place in the primary anoxic reactor using wastewater organic compounds as electron donors. The contact reactor is sized and operated to remove biochemical oxygen demand (BOD) while limiting nitrification. This is possible since the nitrification rate is significantly slower than the COD uptake rate in the reactor. In the PN/CD process, almost all nitrification is carried out in two side-stream reactors: the recycle reactor, which receives return activated sludge from the secondary clarifier, and the *recirculation reactor*, which receives recirculated mixed liquor from the primary anoxic reactor as well as recycle reactor effluent. A key characteristic of the process is that the degree of nitrification is controlled *hydraulically*, through variation of the flow rate of mixed liquor from the primary anoxic reactor to the recirculation reactor. Figure 2-13 indicates that the extent of nitrification is directly proportional to the rate of recirculation, since mixed liquor from the primary anoxic [illegible] is the principal input of ammonia to the [illegible]or, i.e., at low recirculation rates, [illegible]ation is achieved (Fig. 2-13a), whereas at high recirculation rates, more nitrification is achieved (Fig. 2-13b). Earlier, Gujer and Jenkins (1975) recognized the ability of the contact stabilization process to achieve a variable degree of nitrification through manipulation of the sludge recycle rate. The present design improves upon this concept by decoupling operation of the secondary clarifier from control of nitrification.

The secondary anoxic reactor is included in the flow scheme following the contact reactor to remove nitrate produced in the contact reactor or carried over from the primary anoxic reactor. A final $N_2$-stripping reactor is not included in the flow scheme. This is because the PN/CD process is designed to remove virtually all oxidized nitrogen from the mixed liquor before it is transferred to the secondary clarifier. Hence, floating sludge due to denitrification in the sludge blanket of the secondary clarifier should not be a problem. PN/CD final effluent may require aeration if discharge standards specify a minimum dissolved oxygen (DO) level.

a. Low recirculation rate → Less nitrification



b. High recirculation rate → More nitrification

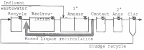


Figure 2-13. Effect of mixed liquor recirculation rate on nitrification in the PN/CD process

## Modeling of Single-sludge Processes for Nitrogen Removal

The International Association of Water Quality published in 1987 a model for activated sludge, the Activated Sludge Model 1 (ASM-1) (Henze et al., 1987). This model has become widely accepted for modeling activated sludge processes, especially those involving nitrogen removal (Bidstrup and Grady, 1988, Hamilton et al., 1991, Jain et al., 1991, [illegible] et al., [illegible]; Stamou, 1994). The ASM-1 depicts seven biochemical processes that take place in the activated sludge process. These include (1) aerobic heterotrophic growth, (2) anoxic heterotrophic growth, (3) aerobic autotrophic (nitrifier) growth, (4) decay of heterotrophs, (5) decay of autotrophs, (6) ammonification of soluble organic nitrogen, (7) hydrolysis of particulate organic matter, and (8) hydrolysis of particulate organic nitrogen. There are a total of 13 process variables, including soluble and particulate inert organics ($S_I$, $X_I$), soluble and particulate degradable organics ($S_S$, $X_S$), heterotrophic and autotrophic biomass ($X_{B,H}$, $X_{B,A}$), particulate products from biomass decay ($X_P$), nitrate+nitrite nitrogen ($S_{NO}$), ammonia nitrogen ($S_{NH}$), soluble and particulate degradable organic nitrogen ($S_{ND}$, $X_{ND}$), dissolved oxygen ($S_O$), and alkalinity ($S_{ALK}$). The first seven components are expressed in units of chemical oxygen demand (COD), the nitrogen species are expressed in terms of their nitrogen content, dissolved oxygen is expressed as negative COD, and alkalinity is given in terms of moles $HCO_3^-/m^3$. Detailed descriptions of the ASM-1 model biokinetic rate equations may be found elsewhere (Dold and Marais, 1986; Henze et al., 1987; Bidstrup and Grady, 1988).

The ASM-1 contains 5 stoichiometric and 14 kinetic parameters. These are identified and typical values given

[illegible]

[illegible] Most of these were reported by the IAWQ Task Group (Henze et al., 1987) and are based on an exhaustive review of the modeling literature. The maximum specific growth rate of autotrophic (nitrifier) biomass and ammonia half-saturation coefficient for autotrophic growth were estimated experimentally using wastewater from the Kanapaha Water Reclamation Facility (Antoniou et al., 1990, Hamilton et al., 1981).

Table 2.2 — ASM-1 kinetic and stoichiometric parameters

| Parameter | Symbol | Value | Typical Units |
|---|---|---|---|
| STOICHIOMETRIC PARAMETERS | | | |
| Yields | | | |
| Heterotrophic | $Y_H$ | 0.67 | mg cell COD/mg COD utilized |
| Autotrophic | $Y_A$ | 0.24 | mg cell COD/mg N utilized |
| Biomass fraction yielding particulates | $f_P$ | 0.08 | dimensionless |
| Composition | | | |
| Mass N/mass COD in biomass | $i_{XB}$ | 0.086 | mg N/mg COD |
| Mass N/mass COD in biomass products | $i_{XP}$ | 0.06 | mg N/mg COD |
| KINETIC PARAMETERS | | | |
| Maximum Specific Rates | | | |
| Heterotrophic Growth | $\mu_H$ | 5.2 | day |
| Autotrophic Growth | $\mu_A$ | 0.41 | day |
| Rate Coefficients | | | |
| Hydrolysis | $k_h$ | 2.4 | mg particulate COD / (mg cell COD-day) |
| Ammonification | $k_a$ | 0.07 | L/(mg cell COD-day) |
| Heterotrophic Decay | $b_H$ | 0.5 | day |
| Autotrophic Decay | $b_A$ | 0.1 | day |
| Half Saturation Coefficients | | | |
| Substrate Coeff. for Heterotrophs | $K_S$ | 20 | mg COD/L |
| Nitrate Coeff. for Heterotrophs | $K_{NO}$ | 0.5 | mg NO -N/L |
| Ammonia Coeff. for Autotrophs | $K_{NH}$ | 0.2 | mg $NH_4$ N/L |
| Oxygen Coeff. For Heterotrophs | $K_{O,H}$ | 0.2 | mg COD/L |
| Oxygen Coeff. For Autotrophs | $K_{O,A}$ | 0.4 | -mg COD/L |
| Hydrolysis of Particulate Organics | $K_X$ | 0.024 | mg particulate COD / (mg cell COD) |
| Anoxic Correction Factors | | | |
| for $\mu_H$ (heterotrophic growth) | $\eta_g$ | 0.7 | dimensionless |
| for Hydrolysis | $\eta_h$ | 0.4 | dimensionless |

(Antoniou et al., 1990; Hamilton et al., 1991)

# CHAPTER 3
# NITROGEN REMOVAL IN A PARTIAL NITRIFICATION/COMPLETE DENITRIFICATION PROCESS

## Introduction

A novel single-sludge partial nitrification/complete denitrification (PN/CD) process proposed by Potter (1993) was evaluated through computer simulations and practiced with a bench scale continuous flow system. Performance of this PN/CD process at varying aerobic (oxic) solids retention times (8 and 11 days) and wastewater feed compositions (raw and settled) was investigated by computer simulations based on the IAWQ Activated Sludge Model I (Henze et al., 1986). Volume and energy requirements of the PN/CD process were compared to those of the Ludzack-Ettinger process (Ludzack and Ettinger, 1962), which is representative of fully nitrifying, single-sludge processes currently used for partial nitrogen removal. PN/CD process performance was experimentally confirmed using a bench scale, continuous flow system that was fed settled domestic wastewater supplemented with acetate and ammonia. The system was operated over a range of mixed liquor recirculation rates to demonstrate the use of this variable for controlling the extent of nitrification. The effect of dissolved oxygen concentration in the oxic reactors was also tested experimentally.

## Process Descriptions

The PN/CD process evaluated in the present research was based on a retrofit design proposed for the Kanapaha Water Reclamation Facility in Gainesville, Florida (Potter, 1993). As shown in Figure 3-1(a), the PN/CD process included a primary anoxic reactor that was divided into two reactors-in-series, an aerated contact reactor, a recycle reactor or recirculation reactor, and a secondary anoxic reactor. A version of the Ludzack-Ettinger (LE) process was used for comparison in the computer modeling study (Fig. 3-1b). It consisted of an anoxic reactor (divided in this study into two reactors-in-series) followed by an oxic reactor and a secondary clarifier. Nitrate was introduced to the anoxic reactor by recirculation of mixed liquor from the oxic reactor and, to a lesser extent, by recycle of activated sludge from the clarifier underflow.

## Modeling and Simulation Methods

A computer simulation model was used to predict performance of the LE and PN/CD processes, with model parameters and wastewater compositions taken from the literature. Reactors were modeled as complete-mix stirred-tank reactors and the secondary clarifier was modeled as an

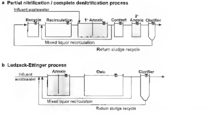


Fig. 3-1. Schematic diagrams of (a) partial nitrification/complete denitrification (PN/CD) process and (b) Ludzack-Ettinger process (Ludzack and Ettinger (1962))

ideal separator. The IAWQ Activated Sludge Model 1 (ASM-1) was used to portray the biochemical reactions in the reactors (Henze et al., 1986). This model includes 13 components (15 including inert nitrogen components) and rate expressions for 8 biochemical processes, including nitrification and denitrification. Detailed descriptions of the ASM-1 biokinetic rate equations may be found elsewhere (Dold and Marais, 1986, Henze et al., 1986; Grady, 1989). The Nelder-Mead algorithm, a nonlinear, multidimensional optimization procedure, was used to find process configurations that minimized total reactor volume (Nelder and Mead, 1965, Press et al., 1989).

## Model Parameters and Wastewater Composition

The ASM-1 contains 5 stoichiometric and 14 kinetic parameters. Parameter values used in simulations were taken from a study of a local facility employing the Ludzack-Ettinger (LE) process and were shown in Table 2-2 in the previous chapter. A temperature of 18°C and pH of 6.8 were used in calculating values of parameters dependent on temperature or pH. Compositions for raw and settled wastewater used in simulations of this project are given in Table 3-1. These component values had been used in other computer simulation works and were used as representative of raw and settled wastewater in this study (Henze et al., 1986, Hamilton et al., 1992).

Table 3.1 — Wastewater compositions used in computer simulations

| Component | | Composition | | Units |
|---|---|---|---|---|
| | | Raw | Settled[b] | |
| Soluble inert substrate | $S_I$ | 20.8 | 25 | mg COD/L |
| Particulate inert substrate | $X_I$ | 102.6 | 25 | mg COD/L |
| Readily degradable substrate | $S_S$ | 96.7 | 70 | mg COD/L |
| Slowly degradable substrate | $X_S$ | 127.4 | 100 | mg COD/L |
| Soluble inert organic N | $S_{NI}$ | 1.5 | 2 | mg N/L |
| Particulate inert organic N | $X_{NI}$ | 2.7 | - - | mg N/L |
| Nitrate plus nitrite N | $S_{NO}$ | 0.0 | 1 | mg N/L |
| Ammonia N | $S_{NH}$ | 22.3 | 10 | mg N/L |
| Soluble degradable organic N | $S_{ND}$ | 8.0 | 5 | mg N/L |
| Particulate degradable organic N | $X_{ND}$ | 3.6 | 10 | mg N/L |
| Active heterotrophic biomass | $X_{B,H}$ | 0.0 | 0 | mg COD/L |
| Active autotrophic biomass | $X_{B,A}$ | 0.0 | 0 | mg COD/L |
| Inert products from decay | $X_P$ | 0.0 | 0 | mg COD/L |
| Alkalinity | $S_{ALK}$ | 5.0 | 5 | mmoles $HCO_3$/L |
| Dissolved oxygen | $S_O$ | 0.0 | 0 | mg COD/L |

Kanapaha Water Reclamation Facility, Gainesville, Florida (Hamilton et al., 1992)

[b] Switzerland (Henze et al., 1986)

Process Performance Evaluation

In process modeling, an influent flow rate of wastewater equal to 37,850 $m^3$/d (10 Mgal/d) and a return sludge recycle ratio (return sludge recycle flow rate divided by influent flow rate) of 1.0 were used. These values are representative of a full-scale Ludzack-Ettinger process used at the Kanapaha Water Reclamation Facility in Gainesville, which also was the plant at which estimates for selected ASM-1 parameters were determined experimentally and raw wastewater was characterized (Hamilton et al., 1991). The target effluent $S_aN$ (the sum of $NH_4$-N, $NO_3$-N, and soluble degradable organic nitrogen) was set at 9.0 mg/L. This was based on an assumed limit of 12 mg/L total N, with an allowance of 3.0 mg/L for effluent particulate nitrogen plus soluble inert organic nitrogen. The latter value takes into consideration an effluent suspended solids concentration of up to 20 mg/L with a nitrogen content of 8%, and a soluble organic nitrogen concentration in the effluent of up to 1.5 mg/L.

A limit of 4000 mg/L was placed on the total suspended solids (TSS) concentration in the clarifier feed. This is representative of process designs for biological nitrogen removal facilities (EPA, 1993). Particulate organic matter, including biomass, in ASM-1 is expressed in terms of COD concentrations. To establish a limit on the mixed liquor suspended solids (MLSS) concentration entering the secondary clarifier, the particulate matter content of the mixed liquor as predicted by the model, had to be converted to the dry weight units appropriate for measurement of MLSS. This was done using a conversion factor ($f_{cv}$) of 1.48 grams COD per gram volatile suspended solids (VSS), as reported by Schroeter et al. (1984), and a typical ratio of VSS/TSS (the volatile fraction, $f_v$) of 0.74. Application of these factors is shown in the equation below.

$$\text{MLSS[mg/L dry weight]} = (X_S + X_I + X_{B,H} + X_{B,A} + X_P)\frac{1}{f_{cv}\ f_v} \qquad (3.1)$$

where $X_S$ = slowly degradable substrate [mg/L COD]

$X_I$ = inert particulate organic substrate [mg/L COD]

$X_{B,H}$ = active heterotrophic biomass [mg/L COD]

$X_{B,A}$ = active autotrophic biomass [mg/L COD]

$X_P$ = inert products from biomass decay [mg/L COD]

The effect of oxic solids retention time (oxic SRT), DO in oxic reactors, and mixed liquor recirculation ratio (mixed liquor recirculation flow rate divided by influent flow rate) on the performance of LE and PN/CD processes treating raw wastewater was first compared. Reactors in the LE process were sized to give the minimum total volume that met the effluent $S_{NH}$ and clarifier feed TSS constraints under base case conditions (oxic SRT = 13 days, DO in oxic reactors = 1.0 mg/L, recirculation ratio = 2.0). The same total reactor volume was used in simulating the PN/CD [illegible]. The total volume was [illegible] as [illegible] recycle reactor = [illegible]%, recirculation reactor = [illegible], primary anoxic reactor = 32.0 (16 for each [illegible]) [illegible] = 1.0%, and secondary anoxic reactor = [illegible]. The effect of oxic SRT (8 vs. 11 days) and wastewater composition (raw vs. settled, as given in Table 3-1) on reactor volume and energy requirements of the LE and PN/CD processes was investigated next. The target $S_N$ was again set at 8.0 mg/L and the influent wastewater flow rate, sludge recycle ratio, oxic reactor DO, and maximum clarifier feed TSS were set as before. The recirculation ratio (m) was set by the optimization algorithm. Energy consumption for aeration, sludge recycle pumping and mixed liquor recirculation pumping was estimated by applying the following unit energy consumption ratios: 1 kWh/kg O transferred, 0.025 kWh/m$^3$ recycle sludge pumped, and 0.016 kWh/m$^3$ mixed liquor pumped for recirculation. These ratios were derived from textbook estimates of aerator, motor and pump efficiencies, combined with assumed total dynamic heads of 1.5 m for sludge recycle pumping and 0.91 m for mixed liquor recirculation pumping (Metcalf & Eddy 1981, 1991).

## Experimental Methods

### Description of the PN/CD Bench Scale System

The bench-scale experimental system employed the same process configuration shown in Figure 3-1a and was sized to give reactor volume ratios identical to those proposed for retrofitting a local Ludzack-Ettinger process to the PN/CD process (Potter, 1993). The wastewater feed rate was 20 mL/min. The system included a 1.63 L aerated recycle reactor, a 5.60 L aerated recirculation reactor, a 3.62 L non-aerated primary anoxic reactor (consisting of two 1.81 L reactors-in-series), a 0.78 L aerated contact reactor, and a 0.78 L non-aerated secondary anoxic reactor. The secondary clarifier had an overall liquid depth of 74 cm and a volume of 5.5 L. It consisted of a 10-cm inside diameter cylinder joined to a conical bottom (17 cm in height). A wire, bent to conform to the inside of the cone, was rotated at 1 rev/min to aid sludge movement.

The reactors were stirred by flat-blade turbines at 180 rev/min. Primary anoxic reactors and the secondary anoxic reactor were covered to limit oxygen intrusion. The secondary anoxic reactor, which is more difficult to prevent air intrusion because of its small volume, was continuously stripped with nitrogen gas to further help in maintaining anoxic conditions. Settled sludge was recycled at a constant rate of 20 mL/min (100% of inflow rate). Oxic reactors were metered using air stored [illegible] compressed gas cylinders. Air was supplied to the [illegible] and recirculation reactors. The contact reactor was initially supplied with air and later switched to oxygen. Aeration was controlled to maintain a target DO. Dissolved oxygen concentration was measured continuously in each aerated reactor using galvanic oxygen electrodes and DO analyzers (New Brunswick Scientific). Gas flow rates to the contact reactor and recirculation reactor were manipulated using mass flow controllers interfaced to a microcomputer that received output from the DO analyzers. The gas flow to the recycle reactor was controlled manually at first and later with a solenoid valve interfaced to the microcomputer.

Domestic wastewater from the University of Florida Water Reclamation Facility was settled for two hours and then supplemented with ammonium sulfate and sodium acetate to bring the ammonia nitrogen and filterable (0.45 µm pore size) COD concentrations to target values which depended on the experiment. The supplemented wastewater was stored at 4°C and was renewed on a weekly basis. Ammonia and acetate were added to the storage tank periodically to restore ammonia nitrogen and COD concentrations to the target values. Feed for the bench scale PN/CD process was pumped directly from the storage tank. Mixed liquor temperature in the reactors was maintained at 23.0 ± 1.5°C.

Influent to the PN/CD system was grab sampled once daily, whereas system effluent was grab sampled three times daily [illegible] composite sample. Subsamples of influent and effluent, before and after filtration through 0.45 µm membrane filters, were acidified and stored at 4°C for up to one week before chemical analysis. This period was well within the maximum 28-day storage period for preserved samples recommended by EPA (1979). The flocculation method of Mamais et al. (1993) was employed to remove colloidal matter prior to analyzing the COD of selected effluent samples. In this method, zinc sulfate ($ZnSO_4 \cdot 7H_2O$) at a concentration of 1000 mg/L was used as a flocculant. The 40 mL sample was dosed with zinc sulfate, mixed with a stirring bar in a 50 mL glass beaker for 1 min, and then settled for 20 min. Supernatant was then passed through a membrane filter having an effective pore size of 0.45 µm (Gelman GN6). Mixed liquor grab samples were taken daily from each reactor and combined in proportion to reactor volume for composite mixed liquor suspended solids (MLSS) determination.

Sludge was wasted on an hourly basis from the secondary anoxic reactor to maintain a target oxic SRT of 11 days. The formula used for computing oxic SRT was:

$$\mathrm{SRT}_{oxic} = \frac{\overline{X}_{oxic} V_{oxic}}{Q_e X_e + Q_w X_w} \qquad (3\text{-}2)$$

where $\overline{X}_{oxic}$ = the volume-weighted composite MLSS of the oxic reactors [mg/L dry weight]

$V$ = total volume of oxic [illegible] [L]

$Q_e$ = effluent flow rate [L/d]

$X_e$ = effluent suspended solids concentration [mg/L dry weight]

$Q_w$ = flow rate of waste activated sludge [L/d]

$X_w$ = concentration of waste activated sludge [mg/L dry weight].

Analytical Methods

Ammonia, nitrite, nitrate and TKN were measured using methods from EPA (1979). Ammonia nitrogen was analyzed using a gas-sensitive electrode (Orion). Nitrite nitrogen was measured by the automated colorimetric method (Technicon). Nitrate nitrogen was measured colorimetrically, following reduction to nitrite using a copper-cadmium reduction column, or by ion chromatograph (Dionex 2000i). TKN was measured by a gas-sensitive electrode after digestion of samples. Total and soluble COD were measured using the COD closed reflux micro method (APHA et al., 1985). Absorbance of the digestate was measured colorimetrically at 420 nm and the COD calculated from a calibration curve.

## Computer Modeling [illegible]

### Effect of Oxic SRT DO and Recirculation Ratio on the LE and PN/CD Processes

Computer modeling results show that effluent ammonia N concentrations in the "partial nitrification" range (e.g., 5-9 mg/L) can be achieved in the LE process over a very narrow range of oxic SRTs (Fig. 3-2a). Continued operation in this range is not feasible because the system is on the verge of washing out the nitrifying bacterial population. In contrast, partial nitrification in the PN/CD process can be achieved over most of the range of oxic SRTs investigated (Fig. 3-2b).

The effect of DO on nitrification in the LE process was similar to that of SRT, i.e., higher DOs caused effluent ammonia to remain low, whereas at low DO effluent ammonia increased sharply (Fig. 3-2c). LE process effluent contained 5-9 mg/L ammonia N over a very small range of DO, making it impractical to maintain partial nitrification using this manipulated variable. The PN/CD process can achieve partial nitrification over a broad range of DO (Fig. 3-2d). Effluent ammonia N in the LE process was not affected by mixed liquor recirculation ratios ranging from zero to four (Fig. 3-2e). In contrast, as mixed liquor recirculation ratio in the PN/CD process was increased, the concentration of effluent ammonia N gradually decreased (Fig. 3-2f). Thus, recirculation ratio offers a convenient

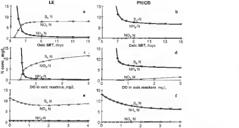


Fig. 3-2 Effect of oxic SRT, dissolved oxygen concentration in oxic reactors, and mixed liquor recirculation ratio on LE and PN/CD processes ($S_tN$: sum of ammonia, nitrate, and readily degradable organic nitrogen; target value of $S_tN$ = 9.0 mg/L)

[illegible] conditions [illegible] PN/CD process

## Volume and Energy Requirements of the LE and PN/CD Processes

Minimum reactor volumes and recirculation ratios needed to achieve the target SₑN of 9.0 mg/L with maximum clarifier feed TSS of 4000 mg/L are given in Table 3-2 for LE and PN/CD processes treating two different wastewaters (raw vs settled) and operating at two different oxic SRTs (8 vs. 11 days). Total anoxic tankage was similar in the two different processes for each combination of oxic SRT and wastewater type. This is reasonable, since even though the two processes nitrify to different extents, each was constrained in the computer modeling procedure to achieve equivalent degrees of nitrogen removal. Biological nitrogen removal is largely through denitrification, hence each process must remove similar quantities of nitrate. Denitrification in both processes is carried out in main stream reactors, therefore it is expected that the denitrification (anoxic) reactor volumes will be similar. The total oxic tankage in the PN/CD process designs was considerably less than in the LE process designs. This advantage derives partly from use of side-stream nitrifying reactors with higher MLSS (and hence, higher reaction rates), and partly from a lesser extent of nitrification. Optimal mixed liquor recirculation ratio in the PN/CD

Table 3-2 — Minimum volume LE and PN/CD processes meeting target effluent $NH_3N$

| Waste-water | Process | Oxic SRT, days | Reactor Volumes m³ Total | Recycle | Recirc | Primary Anoxic | Oxic or Contact | Second Anoxic | Recirc. ratio | Energy Requirements kWh/d Recycle + recirc in | Aeration | [illegible] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raw | LE | 11 | 19,810 |  | - - | 3610 | 16200 | - - | 2.0 | 2160 | 84[illegible] | 10 610 |
|  |  | 8 | 15,360 | – |  | 3050 | 12310 |  | 2.0 | 2160 | [illegible] | 10,160 |
|  | PN/CD | 11 | 13 950 | 4390 | 4700 | 3050 | 810 | 960 | 1.2 | 1670 | [illegible] | 8910 |
|  |  | 8 | 11,300 | 2660 | 4590 | 2460 | 620 | 970 | 1.4 | 1730 | [illegible] | [illegible] |
| Settled | LE | 11 | 8,530 |  | - | 1190 | 7340 |  | 0.6 | 1310 | [illegible] | [illegible] |
|  |  | 8 | 6,760 | – |  | 1000 | 5760 |  | 0.6 | 1310 | [illegible] | [illegible] |
|  | PN/CD | 11 | 4 810 | 1260 | 2380 | 680 | 70 | 420 | 0 | 950 | 5360 | 6310 |
|  |  | 8 | 3 850 | 1100 | 1750 | 660 | 80 | 260 | 0 | 950 | 5070 | 6020 |

Total of the two, equal-volume primary anoxic reactors in series [illegible] on was also lower than in the LE process designs. Lower pumping energy requirements in the PN/CD process reflect its lower recirculation ratios, whereas lower aeration energy requirements of this process reflect its lesser extent of nitrification (Table 3-2).

PN/CD total reactor volume and energy requirements are compared to those of the LE process in Figure 3-3. The total reactor volume required in the PN/CD process was 26 to 44% lower than that required in the LE process for equivalent nitrogen removal (Fig. 3-3, left). SRT had little effect on this relationship. Greater reductions in volume requirements with the PN/CD process were realized with the settled wastewater, as compared to the raw wastewater. This was due to the relatively low concentration of total nitrogen in the settled wastewater (25 mg/L), which enabled the PN/CD process to meet the target $S_{N}N$ with no recirculation of mixed liquor. Consequently, the MLSS concentration in the recirculation reactor equaled that in the return sludge, and the resulting high nitrification rate allowed the necessary degree of nitrification to be achieved with a quite small recirculation reactor volume. With higher influent nitrogen concentrations, the volume savings achieved with the PN/CD process would decline.

Savings in energy consumption with the PN/CD process were 15 to 18% (Fig. 3-3, right). Most of the savings was realized through a decrease in aeration energy requirements as shown in Table 3-2.

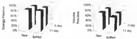


Fig 3-3 Volume and energy requirements of the PN/CD process in relation to type of wastewater and oxic SRT. Left - PN/CD volume as a fraction of LE total volume; right - PN/CD energy consumption as a fraction of LE energy requirements. Total energy requirements included aeration and recirculation plus sludge recycle pumping.

## Experimental Results

A typical profile of ammonia, nitrate and nitrite concentrations in the experimental PN/CD process is shown in Figure 3-4. Ammonia concentration was close to zero in the recycle and recirculation reactors, where nitrification is carried out. Ammonia concentration peaked in the initial zone of the primary anoxic reactor, where influent wastewater was introduced, then decreased slightly through the remaining reactors in the process train. Nitrate nitrogen is produced in the recycle reactor from ammonia introduced with the recycle sludge. Additional nitrate is formed in the recirculation reactor from ammonia brought in with recirculated mixed liquor from the second zone of the

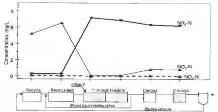


Fig. 3-4. Experimental profile of ammonia, nitrite, and nitrate N in the PN/CD process The profile was taken during phase c of the experimental period

primary anoxic reactor. Nitrate dropped to zero in the primary anoxic reactor, then increased slightly in the contact reactor. This profile shows essentially no further denitrification in the secondary anoxic reactor.

Nine months of performance data from the bench-scale PN/CD process are shown in Figure 3-5. These data demonstrate the effect on process performance of mixed liquor recirculation ratio and DO concentration in the oxic reactors. Mean concentrations of influent soluble COD and ammonia nitrogen over the period shown were 189 mg/L and 26.1 mg/L, respectively. The total concentration of filterable inorganic nitrogen species ($NH_4$-N + $NO_3$-N + $NO_2$-N) in the effluent averaged 8.4 mg/L, of which the major portion (7.5 mg/L on the average) was ammonia. Effluent nitrate + nitrite nitrogen ($NO_x$-N) averaged 1.0 mg/L.

The period of operation shown in Figure 3-5 is divided into six phases. Recirculation ratios of 40%, 75%, 150%, and 400% were investigated during phases a-d, whereas target oxic reactor DO concentrations of 1.0 mg/L and 3.0 mg/L were investigated during phases e and f. The steady-state period of each phase was reached when stable concentrations of effluent ammonia nitrogen, nitrate and nitrite nitrogen, composite mixed liquor suspended solids, and DO in the oxic reactors were observed for over seven consecutive days. Mean wastewater composition, operating conditions and

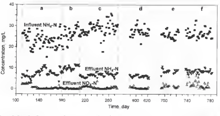


Fig 3 5. Performance of experimental PN/CD process over a total of 9 months of operation. Mixed liquor recirculation ratio was varied in phases a through d [illegible] 40%, 150%, and 400%, respectively). DO concentration in the oxic reactors was [illegible] phases e and f (1 0 mg/L and 3 0 mg/L, respectively) performance are summarized for the steady-state portion of each phase in Table 3-3 and Table 3-4.

Increased recirculation rates were accompanied by a decline in effluent ammonia concentration along with a slight increase in $NO_x$-N concentration (Fig. 3-6). As a net result, the sum of the inorganic nitrogen species decreased with increasing recirculation ratio, leveling above a recirculation ratio of 2.0. Raising the dissolved concentration in the oxic reactors from 1.0 mg/L to 3.0 mg/L had no effect on the mean effluent ammonia nitrogen concentration (Table 3-4). $NO_x$-N concentration increased from 1.4 mg/L to 2.2 mg/L.

## Discussion

Although SRT and DO concentration have strong effects on nitrification rates, neither of these variables is suitable for controlling the extent of nitrification in a nitrogen removal process. The PN/CD process uses side-stream reactors for nitrification and controls the extent of nitrification by manipulating mixed liquor recirculation rates. Other modifications of the contact stabilization and step-feed processes achieve some degree of nitrification in side-stream reactors (Carrio et al. 1993, Cooper et al. 1977, Fillos et al. 1996, Lesouef et al. 1992, Miyaji et al. 1980, Nolasco et al. 1993, 1995, Schlegel 1987, Wanner et

Table 3-3 Influent wastewater composition, operating conditions, and performance of experimental PM/CD process during phases a, b, c and d

| | Phase a<br>(m = 0.75) | | | Phase b<br>(m = 0.40) | | | Phase c<br>(m = 1.50) | | | Phase d<br>(m = 4.00) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | C V * | N** | Mean | C V | N | Mean | C V | N | Mean | C V | N |
| Influent wastewater | | | | | | | | | | | | |
| Filt. COD, mg/L | 213 | (7) | 4 | 204 | (30) | 15 | 230 | (14) | 12 | 248 | (10) | [illegible] |
| TCOD / FCOD | 1.13 | (6) | 3 | 1.62 | (27) | 3 | 1.19 | (6) | [illegible] | [illegible] | [illegible] | [illegible] |
| Total COD, mg/L | 240 | - - | - | 331 | - | - | 274 | - | [illegible] | [illegible] | - | |
| NH4 N, mg/L | 21.6 | (12) | 24 | 26.0 | (13) | 35 | 28.6 | (12) | [illegible] | [illegible] | [illegible] | [illegible] |
| TKN / NH4-N | 1.48 | (21) | 3 | 1.48 | (19) | 3 | 1.09 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| TKN, mg/L | 30.3 | - - | - - | 38.6 | - - | - | 31.2 | | | [illegible] | - | |
| Reactors | | | | | | | | | | | | |
| Composite MLSS[c], mg/L | 2520 | (2) | 24 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| Oxic SRT, days | 10.3 | (22) | 14 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| DO in recycle reactor, mg/L | 1.5[d] | (20) | 14 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| DO in recirc Reactor, mg/L | 1.0 | (8) | 24 | 1.0 | 3 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| DO in contact reactor, mg/L | 0.7[e] | (57) | 24 | 1.1 | (14) | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

[a] m = recirculation ratio

*C V = coefficient of variation in %

**N = number of samples

[b] Nitrate and nitrite concentrations in the influent wastewater were [illegible]

[c] Based on a volume-weighted composite of grab samples from the react[illegible]

[d] Manual DO control, subsequently switched to automatic DO control

[e] Reactor supplied with air (subsequently switched to oxygen)

Table 3.3 continued.

| | Phase a (m = 0.75) | | | Phase b (m = 0.40) | | | Phase c (m = 1.50) | | | Phase d (m = 4.03) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | C.V.* | N** | Mean | C.V. | N | Mean | C.V. | N | Mean | C.V. | N |
| Effluent | | | | | | | | | | | | |
| NH4-N, mg/L | 7.4 | (17) | 24 | 9.7 | (12) | 35 | 6.5 | (13) | 56 | 5.0 | [illegible] | [illegible] |
| NO2-N, mg/L | 0.004 | (265) | 24 | 0.004 | (285) | 35 | 0.02 | (87) | 56 | 0.04 | (61) | [illegible] |
| NO3-N, mg/L | 0.27 | (187) | 24 | 0.22 | (97) | 35 | 0.63 | (86) | 56 | 0.24 | (52) | 21 |
| Tot. inorg. N, mg/L | 7.7 | (16) | 24 | 10.0 | (11) | 35 | 7.1 | (10) | 56 | 6.3 | (9) | 21 |

*C.V. given in %

**N = number of samples

a Based on a volume-weighted composite of grab samples from the reactors

b Manual DO control, subsequently switched to automatic DO control

c Reactor supplied with air (subsequently switched to oxygen)

Table 3-4. Influent wastewater composition, operating conditions, and performance of experimental PN/CD process during phases e and f

| | Phase e (DO = 1.0 mg/L) | | | Phase f (DO = 3.0 mg/L) | | |
|---|---|---|---|---|---|---|
| | Mean | C.V.* | N** | Mean | C.V. | N |
| Influent wastewater | | | | | | |
| Filt. COD, mg/L | 133 | (8) | 11 | 135 | (9) | 21 |
| TCOD / FCOD | 1.40 | (2) | 8 | 1.41 | (5) | 6 |
| Total COD, mg/L | 188 | | — | 190 | | |
| $NH_4$-N, mg/L | 28.4 | (7) | 19 | 28.8 | (9) | 36 |
| TKN / NH4-N | 1.33 | (8) | 8 | 1.33 | (3) | 7 |
| TKN, mg/L | 35.1 | - - | — | 35.4 | - | |
| Reactors | | | | | | |
| Composite MLSS[a], mg/L | 2298 | (2) | 10 | 2289 | (4) | 16 |
| Oxic SRT, days | 10.5 | (3) | 9 | 10.4 | (3) | 16 |
| DO in recycle reactor, mg/L | 1.0 | (8) | 18 | 3.0 | (2) | 36 |
| DO in recirc. reactor, mg/L | 1.0 | (2) | 18 | 3.0 | (1) | 36 |
| DO in contact reactor, mg/L | 1.0 | (1) | 18 | 3.0 | (3) | 36 |
| Effluent | | | | | | |
| $NH_4$-N, mg/L | 8.4 | (6) | 15 | 8.4 | (9) | 36 |
| $NO_2$-N, mg/L | 0.25 | (89) | 18 | 0.55 | (101) | 36 |
| $NO_3$-N, mg/L | 1.1 | (31) | 18 | 1.8 | (60) | 31 |
| Tot. inorg. N, mg/L | 9.8 | (7) | 18 | 10.8 | (17) | 31 |

*C.V. given in %

**N = number of samples

[a] Based on a volume-weighted composite of grab samples from the reactors

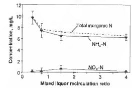


Fig. 3-6 Effect of recirculation ratio on mean effluent ammonia nitrogen and nitrite+nitrate nitrogen concentrations in PN/CD process effluent during steady state periods. Error bars represent ± 1.0 S.D.

al., 1990,). None of these processes control the extent of nitrification by adjusting the mixed liquor recirculation rate, however.

Since nitrification is the predominant factor in the sizing of single-sludge processes for nitrogen removal, the increase in nitrification rates achieved with the higher MLSS in the side-stream reactore enables significant decrease in the oxic tankage. These savings are realized regardless of the oxic SRT and are substantial for either raw wastewater (i.e., high inert content) or settled wastewater (i.e., low inert content). Savings in aeration energy requirements are commensurate with the fraction of influent nitrogen not oxidized, and hence, do not [illegible] either oxic SRT or wastewater composition.

The experimental PN/CD process tested in the [illegible] research removed sufficient nitrogen to give an ef[illegible] inorganic nitrogen concentration in the range of [illegible] 10.0 mg/L. This indicates that the process can readily meet an effluent nitrogen standard of 12 mg/L. The experimental process, consistent with its objective, produced an effluent in which the predominant nitrogen component was ammonia. We demonstrated that by varying the recirculation ratio, both the ammonia nitrogen and the t[illegible] filterable nitrogen concentrations in the effluent could [illegible] controlled. These results are consistent with the prediction of PN/CD process performance obtained using the ASM-1.

An important design feature of the PN/CD process is a very limited extent of nitrification in the contact reactor. From the experimental nitrogen profile presented in Figure 3-4, it is seen that less than 1 mg/L of $NO_x$-N is produced in this reactor. The corresponding nitrogen oxidation rate observed in the contact reactor amounts to 1-2% of the influent TKN loading for this case. In general, effluent $NO_x$-N concentrations were in the range of 0.3 to 2.2 mg/L.

Another important feature of the PN/CD process is its relative insensitivity to the DO concentration of the oxic reactors. This is important, because normal DO fluctuations would not hamper control of the extent of nitrification. The experimental results confirmed model predictions that, above 1 mg/L, DO has little influence on nitrification.

The partial nitrification/complete denitrification process should be considered for nitrogen removal at facilities that must meet an effluent total nitrogen requirement in the range of 10 mg/L or higher and that are not constrained by effluent ammonia limits. Constraints of this type are commonly encountered by plants that use their treated effluent for high-rate irrigation or groundwater discharge. Further experimental work is required to confirm the applicability of the ASM-1 model to describe PN/CD process performance and to characterize the sensitivity of this process to key variables such as the carbon to nitrogen ratio of the influent wastewater which is described in the next chapter.

# CHAPTER 4

# EFFECT OF INFLUENT CHEMICAL OXYGEN DEMAND TO NITROGEN RATIO ON A PARTIAL NITRIFICATION/COMPLETE DENITRIFICATION PROCESS

## Introduction

Single-sludge pre-denitrification processes, such as the Ludzack-Ettinger (LE) process (Ludzack and Ettinger, 1962), have proven effective for partial nitrogen removal from wastewater. In the LE process, influent nitrogen not assimilated into cell mass is almost completely oxidized by nitrifying bacteria to nitrate. Some of the nitrate is biologically reduced to nitrogen gas using wastewater organic matter as electron donor Other single-sludge pre-denitrification processes, for example, the Reaeration-Denitrification-Nitrification (R-D-N) and modified step feed processes, have achieved comparable performance while reducing reactor volume requirements (Cooper et al , 1977, Lesouef et al., 1992, Miyaji et al., 1980, Nolasco et al , 1983, 1985, Schlegel, 1987, Wanner et al , 1990) The modified step feed process also decreases energy requirements relative to the LE process by eliminating mixed liquor recirculation pumping All of these processes are designed and operated to achieve nitrogen removal through complete nitrification and partial denitrification.

An alternative approach to nitrogen removal is the Partial Nitrification/Complete Denitrification (PN/CD) process proposed by Potter (1993). This process is designed to oxidize to nitrate only a fraction of the ammonia and organic nitrogen in the process influent. Essentially all of the nitrate produced is denitrified. In the PN/CD process, less ammonia is oxidized and hence less oxygen is required for any given degree of nitrogen removal as compared to nitrogen removal processes that completely nitrify (e.g., LE, R-D-N, modified step feed). Because the PN/CD process carries out nitrification in return sludge side-stream reactors, it also provides volume savings relative to the LE process (Potter, 1993). The PN/CD process utilizes a novel means of hydraulically controlling the extent of nitrification. Control is achieved by manipulating the return of ammonia-rich mixed liquor from a pre-anoxic reactor to a side-stream nitrification reactor. Neither the LE, R-D-N, nor modified step feed process seek to control the extent of nitrification other than to nitrify to the greatest extent possible.

A critical variable in the performance of single-sludge pre-denitrification processes is the composition of the influent wastewater. Low ratios of biodegradable organic matter to nitrogen can lead to poor biological nitrogen removal because of electron donor limitation of heterotrophic denitrifying bacteria (Narkis et al., 1979, Sutton et al., 1975). The minimum ratio at which complete denitrification is achieved was found by Narkis et al. (1979) to be 2.3 grams soluble BOD per gram nitrate nitrogen, based on studies using post-denitrification and pre-denitrification processes. Sutton et al. (1979) reported that approximately 8 grams filterable chemical oxygen demand (COD) must be available for each gram nitrate nitrogen reduced in order to achieve complete denitrification in the anoxic reactors of pre-denitrification processes. The requirement found by Sutton et al. (1979) is high relative to the ratio of 3.7 grams COD consumed/gram nitrate nitrogen reduced that was reported by McCarty et al. (1969). This was attributed to the rapid initial adsorption of COD by activated sludge in the anoxic reactor.

Although the influence of wastewater composition has been extensively studied for completely nitrifying pre-denitrification processes, no such work has been carried out for processes designed to partially nitrify and completely denitrify. Accordingly, the objective of this study was to experimentally determine the effect of influent COD/N ratio on the performance of a bench-scale PN/CD process. Sensitivity of process performance to influent ammonia concentration was also considered.

## Materials and Methods

### Process Operation

The experimental PN/CD process was set up as described previously. The wastewater feed rate to the process was 20 mL/min. Underflow from the secondary clarifier was recycled at a constant rate of 20 mL/min (100% of inflow rate). Mixed liquor was recirculated from the second of the two primary anoxic reactors in-series to the recirculation reactor at a rate of 30 mL/min (150% of the inflow rate). Sludge was wasted on an hourly basis from the secondary anoxic reactor. The oxic solids retention time (oxic SRT), which was based on aerated reactor sludge inventory, was maintained at 10.7 days. Mean liquid temperatures during seven different phases of operation ranged from 21.5 to 25.0°C.

Oxic reactors were aerated using air stones connected to compressed gas cylinders. Oxygen was supplied to the contact reactor, and air or oxygen to the recycle and recirculation reactors. Aeration was controlled to maintain a target DO of 1.0 mg/L. Dissolved oxygen concentration was measured continuously in each aerated reactor using galvanic oxygen electrodes and DO analyzers (New Brunswick Scientific). Gas flow rates to the contact and recirculation reactors were manipulated using mass flow controllers interfaced to a microcomputer that received output from the DO analyzer. The gas flow to the PN/CD reactor was controlled with a solenoid valve interfaced to the microcomputer.

Operation of the PN/CD system was divided into seven phases with different target ratios of influent COD to influent TKN. (Because the influent wastewater contained no nitrate, the ratio of influent COD to influent TKN will be referred to as the COD/N ratio.) Operation in each phase was continued until one week or more of approximately steady-state performance was achieved. The process was fed domestic wastewater from the University of Florida Water Reclamation Facility. After collection, the wastewater was settled for two hours and then supplemented with ammonium sulfate and sodium acetate as appropriate to reach target concentrations of ammonia and COD. The supplemented wastewater was stored at 4°C and was refilled on a weekly basis. Ammonia and acetate were added to the storage tank periodically to restore ammonia nitrogen and COD concentrations to the target values. Sodium bicarbonate was added to the storage tank at the lower COD/N ratios in order to prevent pH in the bioreactors from dropping below 6.8. Wastewater feed was pumped from the refrigerated storage tank directly to the bench scale PN/CD process.

## Sampling and Analytical Methods

Influent to the PN/CD system was grab sampled once daily. System effluent was grab sampled three times daily to give a composite sample. Aliquots of the samples were acidified and stored at 4°C for up to one week prior to analysis of ammonia, nitrate, and nitrite, and up to one month before analysis of total Kjeldahl nitrogen, which is consistent with the maximum 28-day holding period for preserved samples recommended by EPA (1979). COD and total suspended solids were measured on fresh samples. The flocculation method of Mamais et al. (1993) was employed to remove colloidal matter prior to analyzing the COD of selected influent and recycle reactor samples. Samples were settled prior to flocculating the supernatants. Flocculated COD of recycle reactor mixed liquor was used as an estimate of soluble inert COD in process effluent. It was assumed that virtually all soluble, biodegradable organic matter in this reactor would have been consumed. Mixed liquor grab samples were taken from each reactor daily and combined in proportion to reactor volume to give a composite mixed liquor sample. Mixed liquor suspended solids (MLSS) analysis was performed on this sample.

Ammonia, nitrate, nitrite and TKN were measured using methods from EPA (1979). Ammonia nitrogen was analyzed using a gas-sensitive electrode (Orion). Nitrite nitrogen was measured by the automated colorimetric method technique). Nitrate nitrogen was measured by [illegible] methods: colorimetrically following reduct[illegible] with a copper-cadmium column (samples cont[illegible] mg/L NO -N), ion chromatography using a Dione[illegible] (samples containing 2 mg/L $NO_3$-N or higher), or the [illegible] test 'N tube (chromotropic acid) method for samples from the last phase of operation. TKN was measured by colorimetric method after digestion (EPA, 1979). COD was measured using the COD closed reflux micro method (APHA et al. 1985). Absorbance of the digestate was measured colorimetrically at 420 nm and the COD concentration was calculated from a calibration curve which was prepared for each new lot of COD vials (Hach). The pH in each reactor was measured periodically. Filterable COD (FCOD) was analyzed on samples filtered through membrane filters with 0.45 µm effective pore size (Gelman GN-6).

## Results and Discussion

Performance data spanning 13 months of operation of the bench-scale PN/CD process are shown in Figure 4-1. Operation was divided into seven phases with differing target COD/N ratios. The high values of effluent ammonia nitrogen (11-17 mg/L) seen on days 272 to 278 were caused by low pH (as low as 6.1) in the recycle and recirculation reactors. This resulted from low influent alkalinity (68 to 114 mg/L as $CaCO_3$) in combination with a low influent COD/N

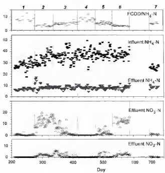


Fig 4-1. Daily performance of experimental FN/CD process operation over a period of 13 months. The seven phases of operation are indicated by the numbers at the top of the figure.

ratio that limited recovery of alkalinity from denitrification Subsequently, sodium bicarbonate was added to the influent wastewater reservoir in order to maintain a minimum reactor pH of 6.8.

The [illegible] of effluent ammonia concentrations in the bench-scale PN/CD process was relatively small. This can be seen from frequency distributions of influent and effluent ammonia concentrations (Fig. 4-2). Influent ammonia nitrogen concentrations for all data averaged 34.6 mg/L with 95% of the values falling between 24 and 47 mg/L. The mean effluent ammonia concentration was 7.8 mg/L, and 95% of the effluent ammonia concentrations were in the range of [illegible] to 11 mg/L. Effluent ammonia concentration was insensitive to influent ammonia ammonia concentration. For example, in phase 1 the unit variation of effluent ammonia with respect to influent ammonia was 10% (Fig. 4-3). Unit variations in the remaining phases ranged from 7% to 19%, and the average of all phases was 14%.

The influent ratio of filterable COD (FCOD) to $NH_3$-N had no effect on effluent FCOD concentration over the range investigated (Fig. 4-4). A slightly decreasing trend in effluent ammonia with increasing influent FCOD/$NH_3$-N ratio was observed. This is consistent with increased N assimilation that would be expected at higher relative COD concentrations due to increased production of biomass.

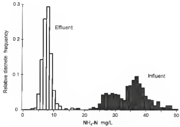


Fig. 4-2. Relative discrete frequency distributions of influent and ef[illegible] nitrogen concentrations over the 13 month operating period. A 1.0 mg/l [illegible] used

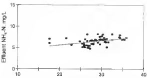


Fig 4-3 Effluent ammonia N concentration versus influent ammonia N concentration during the first phase of operation (mean influent $FCOD/NH_4$-N = 8.3). The indicated linear relationship has a slope of 0.099 and $r^2$ of 0.16 (N = 66).

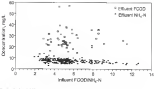


Fig. 4-4. Effluent FCOD and ammonia N concentrations versus influent $FCOD/NH_4$-N ratio over the 13 month operating period.

Representative profiles of nitrogen species concentrations obtained at low (4.3) and high (7.5) influent COD/N ratios are shown in Figure 4-5. Both sets of profiles illustrate that ammonia recycled from the clarifier and recirculated from the primary anoxic reactor was completely oxidized in the side-stream (recycle and recirculation) reactors. The influent COD/N ratio had no effect on the ammonia profile but strongly influenced the nitrate and nitrite profiles. At the higher influent COD/N ratio (7.5), complete denitrification was achieved in the primary anoxic reactor. At the lower COD/N ratio (4.3), limited denitrification was achieved in the primary anoxic reactor. The rate of nitrification in the contact reactor, as measured by ammonia removal, ranged from 6 to 12% of the rate that ammonia was input to the PN/CD process via influent wastewater.

Summaries of process performance under approximately steady-state conditions are given in Tables 4-1, 4-2, and 4-3. Each phase of operation was continued until the effluent nitrate, nitrite, and ammonia nitrogen concentrations reached steady values for eleven days or more. Data from these periods were used for computing the averages and coefficients of variation (C.V.) shown in the performance summaries.

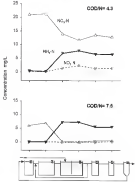


Fig. 4-5. Profiles of nitrogen species concentrations in completely mixed reactors of bench-scale PN/CD process at high and low influent COD/N ratios.

Table 4 [illegible] conditions and [illegible]

| | Phase 1 | | | Phase | | |
|---|---|---|---|---|---|---|
| | Mean | C.V.[a] | N | Mean | C.V. | [illegible] |
| Infl FCOD, mg/L | 237 | 15 | 14 | 114 | 1 | [illegible] |
| TCOD/FCOD | 1.29 | 9 | 2 | 1.51 | 8 | [illegible] |
| Total COD[b], | 355 | -- | -- | 171 | -- | -- |
| Flocc | 0.89 | 6 | 3 | 0.751 | 10 | [illegible] |
| Flocc COD[c] | 213 | - | - - | 86 | | |
| $NH_4$-N, mg/L | 28.6 | 12 | 66 | 35.6 | 1[illegible] | [illegible] |
| TKN / $NH_4$ N | 1.09 | 5 | 3 | 1.12 | 7 | [illegible] |
| TKN[d], mg/L | 31.2 | - - | - - | 40.0 | | |
| TCOD / TKN | 5.8 | - - | - - | 4.3 | -- | |
| Reactor Temp °C | 21.5 | 6 | 66 | 25.0 | [illegible] | [illegible] |
| MLSS[e], mg/L | 2750 | 5 | 63 | 1478 | 10 | [illegible] |
| Oxic SRT, days | 10.7 | 4 | 63 | 10.9 | 5 | [illegible] |
| Recycle DO | 1.0 | 10 | 65 | 1.0 | 4 | [illegible] |
| Recirc DO, | 1.0 | 10 | 65 | 1.1 | [illegible] | [illegible] |
| Contact DO, | 1.1 | 27 | 65 | 1.1 | 20 | [illegible] |
| Effl FCOD, mg/L | 26 | 41 | 3 | 20 | 37 | [illegible] |
| Flocc COD / | 0.74 | 17 | 3 | 0.771 | 24 | [illegible] |
| Flocc COD[f] | 19 | -- | -- | 16 | -- | -- |
| $NH_4$ N, mg/L | 6.5 | 13 | 66 | 5.2 | 11 | [illegible] |
| $NO_2$-N, mg/L | 0.0 | 93 | 66 | 1.7 | 35 | [illegible] |
| $NO_3$-N, mg/L | 0.7 | 99 | 66 | 13.9 | 25 | [illegible] |
| TIN[g], mg/L | 7.2 | 10 | 66 | 23.6 | 11 | [illegible] |

[a] Coefficient of Variation

[b] = mean TCOD/FCOD × mean influent FCOD

[c] = mean influent flocculated COD/FCOD × mean influent FCOD

[d] = mean influent TKN/$NH_4$-N × mean influent $NH_4$-N

[e] Volume weighted composite of MLSS in each reactor

[f] = mean effluent flocculated COD/FCOD × mean effluent FCOD

[g] Total inorganic nitrogen ($NH_4$-N + $NO_2$-N + $NO_3$-N)

Table 4-2 Experimental conditions and system performance

| | Phase 3 | | | Phase 4 | | |
|---|---|---|---|---|---|---|
| | Mean | C.V.[a] | N | Mean | C.V. | N |
| Infl. FCOD, mg/L | 185 | 11 | 12 | 302 | 12 | 6 |
| TCOD/FCOD | 1.37 | 14 | 10 | 1.15 | 8 | 4 |
| Total COD[b], | 253 | - - | - - | 348 | | |
| Flocc | 0.86 | 6 | 6 | 0.94 | 2 | 5 |
| Flocc. COD | 163 | - - | - | 286 | | |
| $NH_4$-N, mg/L | 35.6 | 16 | 34 | 38.4 | 10 | 11 |
| TKN / $NH_4$-N | 1.23 | 9 | 4 | 1.14 | 14 | 8 |
| TKN[d] mg/L | 44.1 | - - | - | 43.9 | | |
| TCOD / TKN | 5.7 | - - | - - | 7.9 | - | |
| Reactor Temp., °C | 22.0 | 1 | 34 | 22.2 | 2 | 59 |
| MLSS[e], mg/L | 1920 | 5 | 23 | 3509 | 3 | 6 |
| Oxic SRT, days | 10.2 | 8 | 23 | 10.6 | 5 | 6 |
| Recycle DO, | 1.0 | 2 | 34 | 1.0 | 5 | 59 |
| Recirc. DO, | 1.1 | 8 | 34 | 1.1 | 7 | 59 |
| Contact DO, | 1.0 | 1 | 34 | 1.0 | 8 | 59 |
| Effl. FCOD mg/L | 23 | 13 | 5 | 35 | 41 | 4 |
| Flocc. COD / | 0.86 | 6 | 5 | 0.63 | 25 | 4 |
| Flocc. COD[f], | 19 | | | 22 | - - | - - |
| $NH_4$-N, mg/L | 7.9 | 18 | 34 | 7.5 | 9 | 11 |
| $NO_2$-N, mg/L | 0.3 | 184 | 34 | 0.0 | 185 | 11 |
| $NO_3$-N, mg/L | 0.8 | 55 | 34 | 0.1 | 81 | 11 |
| TIN[g] mg/L | 9.1 | 18 | 34 | 7.6 | 9 | 11 |

[a] Coefficient of variation

[b] = mean TCOD/FCOD × mean influent FCOD

[c] = mean influent flocculated COD/FCOD × mean influent FCOD

[d] = mean influent TKN/$NH_4$-N × mean influent $NH_4$-N

[e] Volume weighted composite of MLSS in each reactor

[f] = mean effluent flocculated COD/FCOD × mean effluent FCOD

[g] Total inorganic nitrogen ($NH_4$-N + $NO_2$-N + $NO_3$-N)

[illegible] sten p [illegible]

| | Phase | | | Phase | | | [illegible] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | [illegible] | N | Mean | C V | [illegible] | [illegible] | [illegible] | [illegible] |
| Infl [illegible] | 202 | [illegible] | [illegible] | 121 | 8 | [illegible] | [illegible] | | [illegible] |
| TCOD/FC[illegible] | 1 270 | [illegible] | [illegible] | 1 380 | 7 | 5 | [illegible] | | [illegible] |
| Total COD | 757 | – | | 167 | – – | – | [illegible] | | |
| Flo c | 0.881 | [illegible] | 5 | 0.811 | 9 | [illegible] | [illegible] | [illegible] | [illegible] |
| Flocc COD$^{c}$, | 178 | [illegible] | | 98 | | | [illegible] | | |
| $NH_4$ N, mg/L | 38 [illegible] | [illegible] | 37 | 37 7 | 7 | [illegible] | [illegible] | | [illegible] |
| TKN / $NH_4$-N | 1 290 | 20 | 8 | 1 182 | 39 | [illegible] | [illegible] | [illegible] | [illegible] |
| TKN$^{d}$, mg/L | 58.2 | | | 44 6 | | | [illegible] | | |
| TCOD TKN | 5 1 | | | 3 7 | | | [illegible] | | |
| Reactor Temp , °C | 24 0 | 1 | 37 | 23 9 | 1 | [illegible] | [illegible] | [illegible] | [illegible] |
| MLSS$^{e}$, mg/L | 2399 | 4 | 25 | 1663 | 5 | 14 | [illegible] | | [illegible] |
| Oxic SRT, days | 10 7 | 7 | 24 | 10 7 | 9 | [illegible] | [illegible] | [illegible] | [illegible] |
| Recycle DO, | h | | | 1 0 | 15 | 30 | [illegible] | [illegible] | [illegible] |
| Recirc DO, | h | | | 1 1 | 10 | [illegible] | [illegible] | [illegible] | [illegible] |
| Contact DO, | h | | | 1 0 | 18 | [illegible] | [illegible] | [illegible] | [illegible] |
| Effl FCOD, mg/L | 35 | 9 | 5 | 26 | 15 | 5 | 23 | [illegible] | [illegible] |
| Flocc COD / | 0 788 | 7 | 5 | 0 560 | 29 | 5 | 0 681 | [illegible] | [illegible] |
| Flocc COD$^{f}$, | 28 | | | 14 | | | 15 | | |
| $NH_4$ N mg/L | 7 5 | 13 | 37 | 7 7 | 22 | 30 | 0 4 | [illegible] | [illegible] |
| $NO_2$-N, mg/L | 0 8 | 197 | 37 | 2 5 | 31 | 30 | 0 3 | 8 | [illegible] |
| $NO_3$ N, mg/L | 2 2 | 84 | 37 | 12 9 | 12 | 30 | 1 1 | [illegible] | [illegible] |
| TIN$^{g}$, mg/L | 10 5 | 26 | 37 | 23 0 | 10 | 30 | 9 8 | [illegible] | [illegible] |

[a] Coefficient of variation

[b] mean TCOD/FCOD ÷ mean influent FCOD

[c] mean influent flocculated COD/FCOD ÷ mean influent FCOD

[d] mean influent TKN/$NH_4$-N ÷ mean influent $NH_4$-N

[e] Volume weighted composite of MLSS in each reactor

[f] mean effluent flocculated COD/FCOD ÷ mean effluent FCOD

[g] Total inorganic nitrogen ($NH_4$ N + $NO_2$ N + $NO_3$ N)

[h] Digital DO recording lost; DO controlled using set point of 1 [illegible] as in other periods

[illegible] Mean [illegible] Mean composite MLSS varied [illegible] proportion to the influent COD. Average oxic SRTs were [illegible] in the range of 10.2 to 10.9 days. The mixed liquor recirculation and sludge recycle rates were maintained at constant values for all periods, hence the total SRT was always 137% of the oxic SRT. Mean daily dissolved oxygen concentrations in the oxic reactors (recycle, recirculation and contact) were controlled close to the target value of 1.0 mg/L. Mean effluent FCOD ranged from 20 to 35 mg/L. Estimates of mean filterable biodegradable COD in the effluent (the difference between effluent FCOD and flocculated recycle reactor COD) ranged from 4 to 13 mg/L.

Variation of effluent nitrogen species in relation to influent COD/N ratio is shown in Figure 4-6. The mean effluent ammonia concentration varied little (6.5 to 8.4 mg/L) throughout the range of COD/N applied, and showed no trend. At influent COD/N ratios of 5.3 and higher, mean effluent nitrate plus nitrite nitrogen concentrations were less than 1.5 mg/L and total inorganic nitrogen (TIN) in process effluent was less than 10 mg/L. Lower influent COD/N ratios (3.7 and 4.3) resulted in incomplete denitrification and higher effluent TIN concentrations.

Denitrification performance of the primary anoxic reactor (i.e., pre-anoxic reactor) of the PN/CD process is compared to literature values for pre-anoxic reactor performance in Figure 4-7. A sharp deterioration of [illegible] relative to the input of oxidized nitrogen [illegible] 5 As seen in the figure, [illegible]ion performance of the PN/CD process is [illegible] with other investigators' results

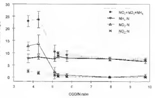


Fig 4-6 Effect of influent COD/N ratio on nitrogen species concentrations in PN/CD process effluent. Error bars represent ± 1 S.D.

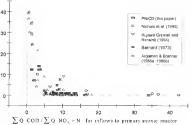


Fig. 4-7. Effect of overall COD/$NO_3$-N ratio of inflows to primary anoxic reactor on $NO_X$-N in primary anoxic reactor.

## CHAPTER 5
## DISCUSSION

It has been shown through model simulations that the PN/CD process offers significant savings in both reactor volume and energy requirements relative to a traditional process for nitrogen removal, the Ludzack-Ettinger process. Furthermore, experimental work has established the ability of the PN/CD to meet effluent targets when treating wastewater having moderately high COD/N ratios, without obvious sensitivity to variations in wastewater composition or DO. Nevertheless, the PN/CD process cannot be feasible at the prototype scale unless it can be successfully operated by wastewater plant personnel. It is argued here that, despite its relatively large number of reactors and unusual flow scheme, the PN/CD process is quite straightforward to operate. This is because the extent of nitrification can be controlled hydraulically (by manipulating mixed liquor recirculation rate), rather than by adjusting aeration rate, oxic volume fraction, or solids residence time. Since the primary anoxic reactors are designed to denitrify all nitrate that reaches them, the overall removal of nitrogen will be a direct function of how much ammonia is oxidized.

This is analogous to the [illegible] process by varying the mixed liquor [illegible]

Examination of Table 5-1 below can further aid in understanding and appreciating the PN/CD process layout. This table gives input and output concentrations of nitrogen species for each of the five reactors in the process. It was developed using experimental data collected when the sludge recycle ratio was 1.0 and the mixed liquor recirculation ratio was 1.5.

Table 5-1 Inorganic nitrogen species concentration in each reactor of PN/CD process (Operating conditions were as follows: influent COD/N=7.5, influent $NH_4$-N = 27.6 mg/L, influent $NO_2$-N + $NO_3$-N = 0.0 mg/L, recirculation ratio = 1.5, sludge recycle ratio = 1.0)

| | Recycle | | Recirc | | 1° Anoxic-a | | 1° Anoxic-b | | Contact | | 2° Anoxic | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | in | out | in | out | in | out | in | out | in | out | in | out |
| $NH_4$-N | 6.22 | 0.27 | 6.87 | 0.27 | 27.6 | 7.18 | 7.18 | 6.87 | 6.87 | 6.32 | 6.32 | 6.22 |
| $NO_2$-N | 0.02 | 0.07 | 0.03 | 0.06 | 0 | 0 | 0 | 0.03 | 0.03 | 0.05 | 0.05 | 0.02 |
| $NO_3$-N | 0.84 | 5.21 | 0.1 | 6.52 | 0 | 0.07 | 0.07 | 0.1 | 0.1 | 0.84 | 0.84 | 0.84 |

Examining ammonia first of all, it is clear that the recycle and recirculation reactors are the major sites of nitrification. The main source of ammonia for the recycle reactor is return sludge from the clarifier underflow, whereas the main source of ammonia for the recirculation reactor is the primary anoxic reactor, which receives the wastewater input. The difference between the influent and effluent ammonia concentrations in the first half of the primary anoxic reactor (1° Anoxic-a) is due almost [illegible] to dilution by ammonia-free mixed liquor from the recirculation reactor. Changes of less than 1 mg/L ammonia concentration are observed in the next three reactors (1° Anoxic-a, contact, 2° Anoxic).

Substantial nitrate production takes place in the recycle and recirculation reactors, whereas almost complete removal of nitrate is achieved in the primary anoxic reactor. Hence, it is seen that essentially all of the nitrate produced is removed. Further changes in nitrate concentration in the contact and secondary anoxic reactors are minor. Nitrite concentrations remain consistently less than 0.1 mg/L in this case. Thus, it is seen that the workhorse reactors of the PN/CD process are the recycle, recirculation, and primary anoxic reactors. The contact and secondary anoxic reactors are principally for effluent polishing.

Another way of assessing the role of the PN/CD process in nitrogen removal is to compare its performance to other single-sludge processes. This has been done in Figure 5-1, which was prepared using performance data from 27 single-sludge processes incorporating both nitrification denitrification for nitrogen removal. These 27 plants are classified into five categories: single anoxic zone [illegible] process, periodic aerat[illegible] [illegible] process and oxidation ditches

[illegible] shows the total nitrogen removal [illegible] treatment plant in relation to influent wastewat[illegible] COD/N ratio. Nitrogen removals improve as the influent wastewater COD/N ratio increases. This trend plateaus at about 80-85% when influent wastewater COD/N ratio reaches [illegible] or higher. Below this ratio, nitrogen removal drops dramatically. The PN/CD process appears to follow the same general trend as the other single-sludge processes, reaching a nitrogen removal of 75% with a lower COD/N ratio than some other single-sludge processes.

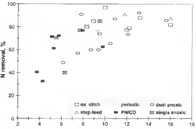


Figure 5.1 Effect of influent COD/N ratio on nitrogen removal in single-sludge processes (see Table 2-1 for references)

# CHAPTER 6
# CONCLUSIONS

Through computer modeling and experimental verification of the PN/CD process, the following conclusions have been reached:

- The PN/CD process should be considered for nitrogen removal at facilities that must meet an effluent total nitrogen requirement in the range of 10 mg/L or higher and that are not constrained by effluent ammonia limits. Experimental results give an effluent inorganic nitrogen concentration in the range of 7.5 to 10.0 mg/L. This indicates that the process can readily meet an effluent nitrogen standard of 12 mg/L.
- The predominant nitrogen species in experimental PN/CD process effluent is ammonia. Both ammonia nitrogen and total filterable nitrogen concentrations in the effluent can be controlled by varying mixed liquor recirculation rates. These results are consistent with the predictions of a biochemical model of the activated sludge process (ASM-1).
- Substantial savings in reactor volume and energy requirements can be realized by substituting the PN/CD process for traditional single-sludge processes that accomplish partial nitrogen removal from wastewater,

such as the Ludzack-Ettinger process. Most of the savings in reactor volume come about because nitrification in the PN/CD process is carried out in side-stream reactors having higher MLSS concentrations than the main-stream reactors. The energy savings are due largely to decreases in aeration energy requirements.

- The PN/CD process can produce relatively constant effluent ammonia concentrations despite variation in influent COD/N ratio and influent $NH_4$-N concentrations.
- Effluent FCOD is not affected by influent FCOD/$NH_4$-N ratios in the range 2 to 11.
- Denitrification in the PN/CD process is nearly complete at influent COD/N ratios of 5.3 or higher. Lower COD/N ratios result in incomplete denitrification.
- Denitrification performance of the pre-anoxic reactor of the experimental PN/CD process is comparable with that achieved in other pre-denitrification processes.
- The PN/CD process is relatively insensitive to the DO concentration of the oxic reactors. Normal DO fluctuations should not hamper control of the extent of nitrification.

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# BIOGRAPHICAL SKETCH

[illegible] Tseng graduated from National Taiwan University in Taiwan and received a Bachelor of Science degree from the Department of Mechanical Engineering in 1985. He spent two years in military service then worked for an engineering firm from 1987 to 1989. He began his graduate studies at the University of Florida in the Department of Environmental Engineering Sciences in January 1990. His major area of study was wastewater treatment, and he received a Master of Engineering degree in environmental engineering in May 1993. After completion of his doctoral degree at the University of Florida in environmental engineering, he plans to work in industry.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ben Koopman, Chair
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gabriel Bitton
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Paul Chadik
Assistant Professor of
Environmental Engineering
Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John Zoltek, Jr.
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Spyros A. Svoronos

Spyros Svoronos
Professor of Chemical
Engineering

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[illegible]

Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School